

Gallia as support of Pt in benzene hydrogenation reaction[☆]

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Abstract

Catalysts of 0.5 wt.% platinum supported on gallia/alumina containing 0, 1, 10 and 100 wt.% of gallia were prepared to study the effects of gallia as a support for the benzene hydrogenation reaction. The catalysts were prepared by the incipient wetness impregnation method with aqueous solutions of H_2PtCl_6 and $\text{Ga}(\text{NO}_3)_3$ as platinum and gallia precursors. $\gamma\text{-Al}_2\text{O}_3$ and $\beta\text{-Ga}_2\text{O}_3$ were used as supports. The following techniques were used to characterize the catalysts: X-ray diffraction, nitrogen adsorption for surface area determination, temperature-programmed reduction, carbon monoxide chemisorption and thermal gravimetric analysis. The benzene hydrogenation was used to test the catalytic activity. The 0.5% Pt/ Al_2O_3 catalyst showed the highest activity. It was observed that the surface area, the dispersion and the activity decreased when the gallia content was increased. The addition of gallia to the alumina did not provide enough acidity to generate isomerization products, since the only reaction product was cyclohexane.

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1. Introduction

The benzene hydrogenation reaction is of great interest in the petroleum industry and environmental protection [1]. Cyclohexane is the precursor for the caprolactam, raw material of nylon 6. Phenol and cyclohexylamine can be prepared from cyclohexane. On the other hand, the existence of excessive amount of aromatics in the kerosene, gasoline and diesel leads to serious air contamination problems. The saturation of the aromatic ring is difficult due to the stabilization of the aromatic ring by resonance. For this reason, benzene hydrogenation has been used as a reaction model to study catalysts for hydrogenation reactions [1,2].

The aim of this work was to study the effect of gallia (gallium oxide, Ga_2O_3) on the catalytic behavior for hydrogenation reactions of platinum supported on alumina. Gallia/alumina supported 0.5% Pt catalysts with different gallia contents, varying from pure alumina to pure gallia, were prepared. The catalysts were characterized by X-ray diffraction

to determinate the phases present on the oxide supports; nitrogen adsorption for surface area determination, pore size and volume by using BET, t -plot and BJH methods; temperature-programmed reduction (TPR) to study the reducibility of the surface species present on the catalyst surface; carbon monoxide chemisorption to evaluate the platinum dispersion and thermogravimetric analysis to determinate the water content. The benzene hydrogenation reaction was used to test the catalytic activity.

2. Experimental

2.1. Catalyst preparation

γ -Alumina (Rhône Poulenc) and β -gallia (Aldrich) were used as catalyst supports, with particle sizes in the range of 60–80 mesh. The supports were calcined at 700 °C for 2 h. Then, two portions of alumina were impregnated with aqueous solutions of $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (Aldrich, 99.9%) to obtain 1 and 10 wt.% of Ga_2O_3 on $\gamma\text{-Al}_2\text{O}_3$. After calcination at 700 °C for 2 h, the supports were impregnated with the appropriate amount of aqueous solutions of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Alpha Products, 40% Pt) to obtain 0.5 wt.% Pt in all catalysts.

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2.2. Techniques

The XRD patterns were recorded using a Philips PW1310 diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$), operating at 36 kV, 20 mA and a 2θ scan rate of $2^\circ/\text{min}$.

Measurements of thermogravimetric analysis (TGA) were carried out on a Mettler Toledo TG 50 thermobalance, equipped with a TC-11 processor. A catalyst sample of 15–30 mg was heated from 35 to 800°C at $20^\circ\text{C}/\text{min}$ under a flow of N_2 ($30 \text{ cm}^3/\text{min}$). The samples were dried overnight at 120°C before analysis.

A Micromeritics Gemini 2375 analyzer was used to determine the surface area, pore size and pore volume, by the BET, t -plot and BJH methods. A sample of 200 mg was dried at 150°C for 1.5 h in a flow of Ar ($20 \text{ cm}^3/\text{min}$) before analysis.

Temperature-programmed reduction (TPR) experiments were carried out in a stainless steel line coupled to a TCD detector. A sample of 100 mg was dried in situ at 120°C for 2 h in a flow of Ar ($30 \text{ cm}^3/\text{min}$). Then, the sample was cooled to room temperature and heated up to 800°C at $10^\circ\text{C}/\text{min}$ in a flow of $30 \text{ cm}^3/\text{min}$ of 5.2% H_2/Ar mixture, recording the signal in a TCD.

In the carbon monoxide chemisorption and benzene hydrogenation, the sample was dried in situ in a flow of Ar ($30 \text{ cm}^3/\text{min}$) at 120°C for 2 h, reduced in a H_2 flow ($30 \text{ cm}^3/\text{min}$) at 400°C for 2 h, followed by cooling to room temperature in the same H_2 flow. A sample of 100 mg was used for CO chemisorption and 20 mg for the benzene hydrogenation. CO pulses of 1.86 mmol were adsorbed at room temperature. The benzene hydrogenation was carried out at 150, 200 and 250°C for 3 h. The $\text{H}_2:\text{C}_6\text{H}_6$ molar ratio was of 14:1. The products were analyzed by gas chromatography using a FID detector.

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 shows the XRD diagrams for all gallia catalysts. The most important signals are summarized in Table 1 and compared to the values reported by Roy et al. [3] for $\beta\text{-Ga}_2\text{O}_3$.

Table 1
XRD data for different samples of Ga_2O_3

Ga_2O_3 fresh		Ga_2O_3 calcined		$\beta\text{-Ga}_2\text{O}_3$	
d	I/I_0	d	I/I_0	d	I/I_0
4.080	73	4.656	68	4.65	60
3.619	56	2.914	99	2.967	100
2.938	52	2.817	88	2.924	100
2.805	54	2.667	87	2.816	100
2.647	100	2.518	100	2.673	60
2.538	57	2.423	87	2.547	100
2.491	80	2.343	67	2.396	80
2.406	56			2.344	80

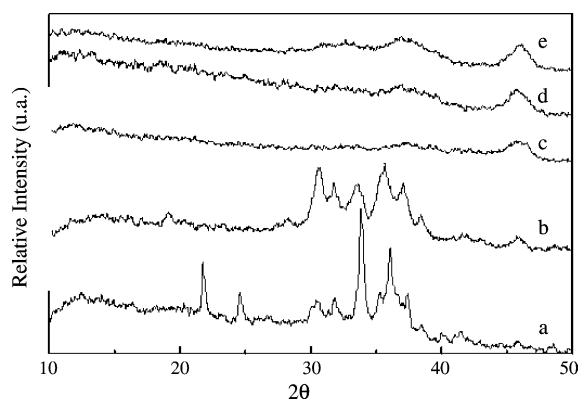


Fig. 1. X-ray diffractogram for (a) Ga_2O_3 (fresh), (b) Ga_2O_3 (calcined), (c) Al_2O_3 , (d) 1% $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ and (e) 10% $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$.

The XRD diffraction pattern of the calcined gallia (Fig. 1b and Table 1) seems to indicate that this sample is β -gallia. In the fresh sample (Fig. 1a) the main peaks of the β -gallia are present and the other peaks disappeared when the sample was subjected to the calcination treatment.

For the samples of pure alumina and alumina covered with 1 and 10% gallia, calcined at 700°C (Fig. 1c–e), no diffraction peaks ascribed to gallia were observed. However, two broad bands unexpectedly appear in the diagrams. These bands are centered at 37.28° and 45.66° for alumina; 37.90° and 45.76° for 1% of gallia and 36.92° and 46.12° for 10% of gallia. These results suggest that these solids have a high amorphous degree and that the gallia can be highly dispersed on the alumina. Other possibilities is that part of the gallium form GaAlO_3 . The peak near 38° has been assigned to these species [4].

3.2. Thermogravimetric analysis (TGA)

Fig. 2 shows the weight loss curves (integral curve) of the catalytic supports. It is clearly observed that the alumina (Fig. 2a) loses weight significantly in a continuous form during the heating, while the gallia (Fig. 2d) has a notably smaller weight loss. All the samples of alumina covered with gallia showed a similar behavior and it is similar to the alumina alone. The increase of the gallia content from 1 to 10% affected very little the weight loss of the alumina sample.

From the weight loss curves the negative first derivative curve of weight can be obtained with regard to the temperature from which the loss of hydration water can be determined. These results are shown in Table 2 and they corroborate the previous results. Zárraga [5] carried out

Table 2
Percentages of weight loss

Sample	% H_2O
Al_2O_3	3.3
1% $\text{Ga}_2\text{O}_3/\text{Al}_2\text{O}_3$	2.7
10% $\text{Ga}_2\text{O}_3/\text{Al}_2\text{O}_3$	2.6
Ga_2O_3	0.4

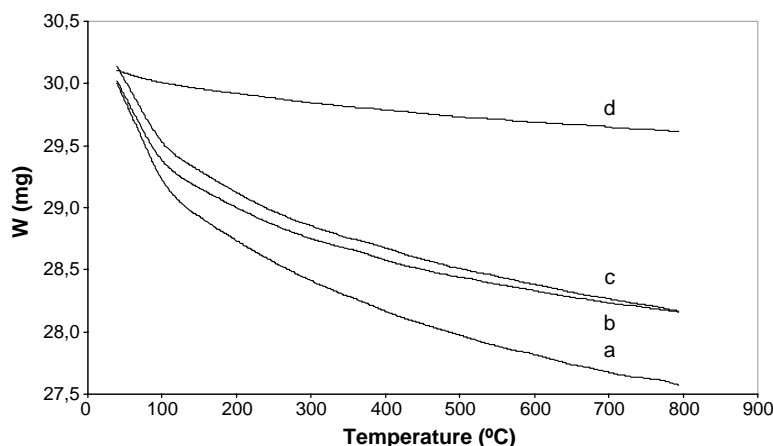


Fig. 2. Thermograms for (a) Al_2O_3 , (b) 10% $\text{Ga}_2\text{O}_3/\text{Al}_2\text{O}_3$, (c) 1% $\text{Ga}_2\text{O}_3/\text{Al}_2\text{O}_3$ and (d) Ga_2O_3 .

Table 3
Surface characteristics of the catalytic supports

Support	S_{BET} (m^2/g)	S_t (m^2/g)	Vol. tot. pores (cm^3/g)	Vol. micropores (cm^3/g)	Average pore radii (\AA)
Al_2O_3	184	172	0.48	0.0047	43.8
1% $\text{Ga}_2\text{O}_3/\text{Al}_2\text{O}_3$	170	155	0.48	0.0062	48.5
10% $\text{Ga}_2\text{O}_3/\text{Al}_2\text{O}_3$	152	140	0.42	0.0050	46.5
Ga_2O_3	19	13	0.05	0.0026	59.2

S_{BET} : surface area (BET); S_t : external surface area.

the temperature-programmed gravimetric desorption over γ - Al_2O_3 samples, and found that the highest loss of water took place at 130 °C and that this corresponds approximately to 3.6% of the original mass, which is similar to that found in this work (3.3%). In our case, the sample was heated at 120 °C for 12 h to eliminate the physisorbed water.

3.3. N_2 adsorption

Table 3 shows the values obtained by the BET, t -plot and BJH methods [6,7]. The value of surface area obtained for the γ -alumina (184 m^2/g) is in good agreement with that reported by other researchers [5,8]. On the other hand, the value of 19 m^2/g obtained for the β -gallia coincides practically with the reported by Okimura et al. [9], of 16 m^2/g , but not with the reported value by Olorunyolemi and Kydd (48 m^2/g) [10]. In another work of the latter author, the gallia phase was identified as α -gallia [11].

In Table 3, it can be appreciated that the alumina presents a surface area significantly higher than the gallia. The surface areas for the alumina recovered with 1 and 10% gallia (170 and 152 m^2/g , respectively) show clearly that this decreases with the increment of gallia content. Nevertheless, a significant effect is not observed in the total pore and micropore volumes of the solids.

The external surface areas (S_t), are 10% lower than that BET area, except for the gallia whose external area is 30% lower than its BET area. With regard to the radii of pore average, it can be said that all the solids are mesoporous

(20 $\text{\AA} < d_p < 500 \text{\AA}$) and the contribution of the micropores is minimum because of the low values of micropore volumes.

3.4. Temperature-programmed reduction

Fig. 3 illustrates the TPR profiles of the studied catalysts. For Pt/ Al_2O_3 catalyst (Fig. 3a) two peaks are observed, at 231 and 388 °C. In the Pt/ Ga_2O_3 catalyst (Fig. 3d) a peak of high intensity appears at 176 °C together with a wide peak at 730 °C. In the case of the mixed catalysts, three peaks are observed in each one. For the 0.5% Pt/1% $\text{Ga}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst (Fig. 3b), these peaks are located at 240, 412 and 582 °C; while for the 0.5% Pt/10% $\text{Ga}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst (Fig. 3c), the same tendency is observed but the peaks have

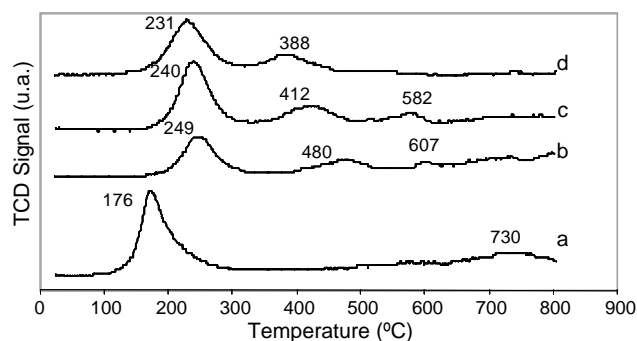


Fig. 3. TPR profiles for Pt supported catalysts: (a) 0.5% Pt/ Ga_2O_3 ; (b) 0.5% Pt/10% $\text{Ga}_2\text{O}_3/\text{Al}_2\text{O}_3$; (c) 0.5% Pt/1% $\text{Ga}_2\text{O}_3/\text{Al}_2\text{O}_3$; (d) 0.5% Pt/ Al_2O_3 .

lower intensity and shifted to higher temperatures: 249, 480 and 607 °C, respectively.

According to Choren et al. [12], the temperature of the first peak and the existence of the second for the 0.5% Pt/Al₂O₃ catalyst (Fig. 3a) are effects of the support, because the reduction of the pure Pt complex occurs in a single step at temperatures in the range of 30–90 °C [13]. These authors also pointed out, based on UV–vis experiments, that the Pt passes from Pt⁴⁺ to Pt⁰ in a single step. On the other hand, Ren-Yuan et al. [14] and Lietz et al. [15], attributed the second peak to the interaction of the Pt with the support, being Pt species strongly adsorbed, but they did not give any evidences for this.

Colina and Medina [16], proposed a different explanation for the occurrence of these peaks. They suggested that the decomposition of the platinum complex occurs in two stages: in the first one, a significant part of the Pt complex is reduced from Pt⁴⁺ to Pt⁰ and a small fraction of Pt⁴⁺ is reduced to Pt²⁺ that interacts strongly with the alumina. The reduction of the latter Pt species would take place at higher temperatures and would explain the occurrence of the second peak.

In the case of 0.5% Pt/Ga₂O₃ catalyst (Fig. 3d), the peak at low temperature corresponds to the reduction of Pt species that interact with the support, while the one at high temperature to gallia.

The effect of gallia addition to the alumina in the catalysts (Fig. 3b and c) is the displacement to higher temperatures of the two peaks observed in 0.5% Pt/Al₂O₃ catalyst, diminishing their intensities with the gallia increment. Jablonski et al. [17], found a similar behavior in the bimetallic catalysts of PtGa/Al₂O₃, suggesting that the modification of the first reduction area could be due to the simultaneous reduction of platinum and a gallium fraction in intimate contact, giving place to PtGa alloys after the reduction. The second reduction peak is attributed to the reduction of gallium separated from the platinum but catalyzed by it. In our case, we propose that the first reduction peak occurs mainly to the reduction of the platinum species as proposed for the Pt/Al₂O₃ catalyst, while the second and third peaks can be due to the reduction of other platinum species and gallia, respectively.

3.5. Carbon monoxide chemisorption

In Table 4 the results of the CO chemisorption are presented. It can be observed that the catalysts of 0.5% Pt/1% Ga₂O₃/Al₂O₃ and 0.5% Pt/Al₂O₃ consume more CO. The CO uptakes are very similar for both catalysts: 0.56 and 0.49 for the CO/Pt ratios, respectively. On other hand, the 0.5%

Table 4
Amount of adsorbed CO on the catalysts

Catalyst	μmol CO _(ads)	CO/Pt
0.5% Pt/Al ₂ O ₃	1.26	0.49
0.5% Pt/1% Ga ₂ O ₃ /Al ₂ O ₃	1.44	0.56
0.5% Pt/10% Ga ₂ O ₃ /Al ₂ O ₃	0.27	0.11
0.5% Pt/Ga ₂ O ₃	0.17	0.06

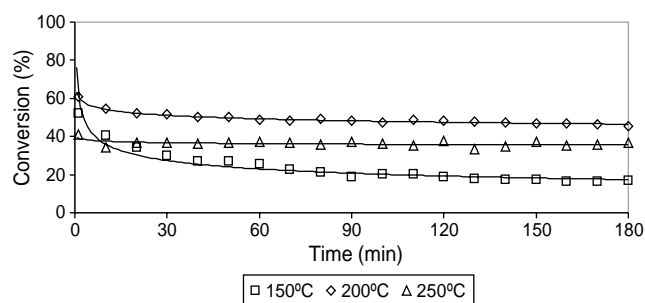


Fig. 4. Conversion as a function of time on-stream for 0.5% Pt/Al₂O₃ catalyst in benzene hydrogenation.

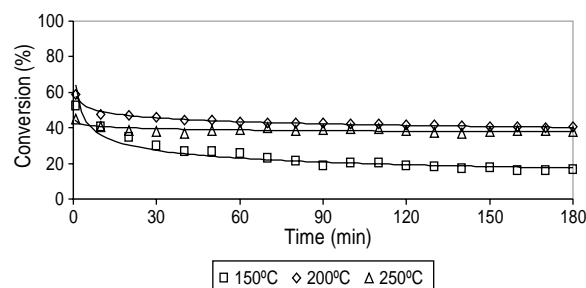


Fig. 5. Conversion as a function of time on-stream for 0.5% Pt/1% Ga₂O₃/Al₂O₃ catalyst in benzene hydrogenation.

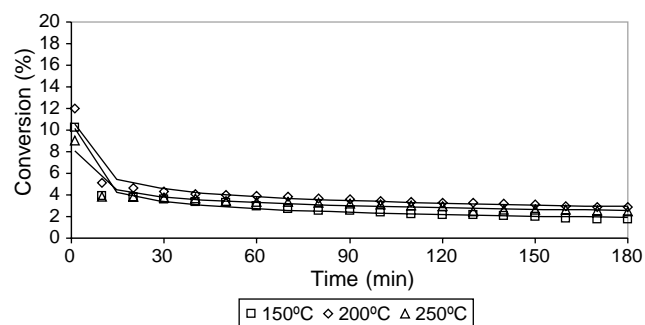


Fig. 6. Conversion as a function of time on-stream for 0.5% Pt/10% Ga₂O₃/Al₂O₃ catalyst in benzene hydrogenation.

Pt/10% Ga₂O₃/Al₂O₃ and 0.5% Pt/Ga₂O₃ catalysts present a significantly lower CO consumption (between 80 and 90% less). The gallia could be promoting a higher dispersion of Pt at low concentrations (1%) but at high concentrations (10%), considering that the surface area diminishes, a smaller dispersion should be obtained, just as it happens.

3.6. Catalytic activity

The activity data obtained for the benzene hydrogenation are shown in Figs. 4–7. Cyclohexane is the only reaction product, as reported by Choren et al. [18] and Wang et al. [19] for Pt/Al₂O₃ catalysts. The former authors found by infrared spectra of adsorbed pyridine in which Pt/Al₂O₃ and Pt/HAl-MCM-41 zeolite catalysts do not have Brønsted acid sites, while Pt/US-SSY zeolite does have Brønsted sites and

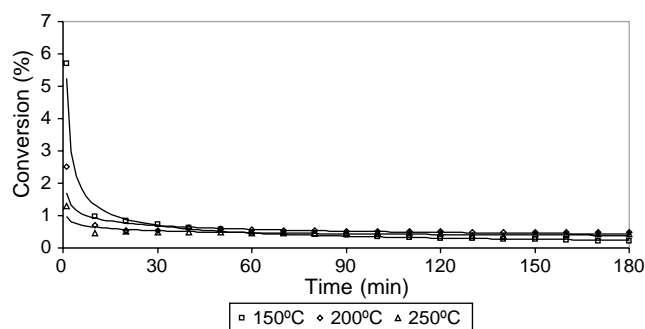


Fig. 7. Conversion as a function of time on-stream for 0.5% Pt/Ga₂O₃ catalyst in benzene hydrogenation.

Table 5
Conversions of benzene for Pt supported catalysts

Catalyst	150 °C		200 °C		250 °C	
	Initial	Final	Initial	Final	Initial	Final
0.5% Pt/Al ₂ O ₃	52.2	16.8	60.8	45.6	41.3	36.6
0.5% Pt/1% Ga ₂ O ₃ /Al ₂ O ₃	52.2	16.8	58.9	40.6	44.9	37.8
0.5% Pt/10% Ga ₂ O ₃ /Al ₂ O ₃	10.2	1.7	11.9	2.9	9.0	2.4
0.5% Pt/Ga ₂ O ₃	5.7	0.2	2.5	0.5	1.3	0.4

methylcyclopentane is formed in the benzene hydrogenation. This could indicate that the gallia, does not provide to the alumina enough Brönsted acid sites to generate isomerization products.

It was observed in all catalysts at each reaction temperature, that the activity diminished with time until reaching stable values. The loss of activity can be attributed to the rapid coke deposition at the early stages of the reaction. The initial and final conversions are summarized in Table 5. The activity results are in line with the dispersion, indicating that the reaction is predominantly occurring on metal sites. On the other hand, considering that the reduction of the catalysts used in this study was carried out at 400 °C and that, according to the TPR profiles, the reduction of gallium species occur at higher temperatures, it is not clear if these species can, somehow, contribute to improve the activity.

It is worth noticing that for a reaction temperature of 250 °C, the activity curve falls among those at 150 and 200 °C. This fact could be related to the following three reasons: proximity to the equilibrium, significant deposition of coke at the beginning of the reaction or diffusion problems. To evaluate these options, the particle sizes were diminished to the range corresponding to 100–200 mesh.

In the first place this new particle size was tested with the 0.5% Pt/10% Ga₂O₃/Al₂O₃ catalyst, obtaining that the activity curves at 150 and 200 °C coincided satisfactorily with the curves of particle size of 60–80 mesh, while that at 250 °C was located above that of 200 °C. This result discards the possibility of thermodynamic limitations at 250 °C, because higher conversions are achieved. Nevertheless, the other two alternatives cannot be discarded when the reaction temperature is 250 °C. Taking this into consideration, experiences were repeated with the particle sizes of 100–200 mesh for the

rest of the catalysts. In accordance with the obtained results, the decrease of the particle size up to 100–200 mesh did not eliminate the diffusional control in all the cases; however, it would be inadequate to reduce the particle size further, because this would bring another series of effects difficult to avoid, for example, a significant increment in the pressure drop. The effect of the coke deposition at higher temperatures is not discarded. For such a reason, the activity data obtained at lower temperatures (150–200 °C) seems to be more useful, since the diffusional control and the coke deposition have a lesser influence at these reaction temperatures.

4. Conclusions

X-ray diffraction for Ga₂O₃/Al₂O₃ samples revealed that the gallia is dispersed on the alumina, and that the calcined gallia corresponds to the β-phase. The increase of gallia content in the alumina reduces the surface area, the dispersion and the activity. The most active catalyst was 0.5% Pt/Al₂O₃, followed by 0.5% Pt/1% Ga₂O₃/Al₂O₃, 0.5% Pt/10% Ga₂O₃/Al₂O₃ and 0.5% Pt/Ga₂O₃. The addition of gallia to the alumina did not provide enough acidity to generate isomerization products. It was not possible to determine neither the effect on the activity of the gallium species reduced at high temperatures nor eliminate diffusional control at reaction temperature of 250 °C, in all the catalysts.

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